Colloidal Release of Plutonium Dioxide from a Ceramic Waste Form

Argonne has developed an electrometallurgical process to convert spent sodium-bonded nuclear reactor fuel into waste forms that can be disposed in a high-level waste repository. One of the waste forms is a ceramic material that consists of about 75 mass% sodalite (incorporating most of the salt), 25 mass% glass binder, and small amounts of halite, clay, and oxides. The qualification of the ceramic waste form (CWF) for disposal requires that ANL identify the physical form and the amounts in which plutonium is released during corrosion of the CWF.

Samples of CWF were prepared with nonradioactive fission product elements as well as the actinides uranium and plutonium. Structural characterization and corrosion tests were performed to determine the effects of uranium and plutonium on the CWF microstructure and corrosion behavior and to determine the release behavior of U and Pu.

The microstructure of the U/Pu-doped CWF was the same as that of nonradioactive CWF with one additional phase. Clusters of polycrystalline 0.020-0.050 μm particles of $(U,Pu)O_2$ were observed within the glass, usually very near glass-sodalite boundaries. Since these $(U,Pu)O_2$ particles could be released into aqueous solution as colloids, corrosion testing of the U/Pu-doped CWF was carried out using the Product Consistency Test (PCT), a test method that exposes a large surface area and that can be used to identify colloids in solution. Crushed, sieved, and washed CWF samples were immersed in demineralized water for 7 days to a year at 90 or 120˚C. Following each test, solutions were removed and passed sequentially through 0.45-μm, 0.10-μm, and 0.005-μm filters. The 0.45-μm filtrates were examined by dynamic light scattering and transmission electron microscopy (TEM).

The main conclusions from these tests were as follows:

- Almost all plutonium is released from U/Pu-loaded CWF as colloidal-sized $(U,Pu)O_2$ particles or as material fixed on test vessel walls. The $(U,Pu)O_2$ particles are usually attached to amorphous aluminosilicate colloids, as shown in the TEM image of material on a holey carbon grid (top figure on next page).

- The releases of matrix elements and trace elements as functions of test duration and temperature were similar to corresponding releases from the nonradioactive CWF.

- The largest fractions of the released plutonium were deposited on vessel walls and in the colloidal size range of 0.005-0.10 μm. The mean normalized releases are shown as a function of particle size range in the bottom figure on the next page.

The corrosion tests of U/Pu-loaded CWF have demonstrated the following:

- Microstructural characterization of heterogeneous waste forms must be carried out prior to corrosion testing in order to guide the choice of corrosion tests and to interpret the results of those tests.

- The techniques of sequential filtration, dynamic light scattering, and TEM are appropriate to characterize colloidal releases from heterogeneous waste forms.

ANL Participants

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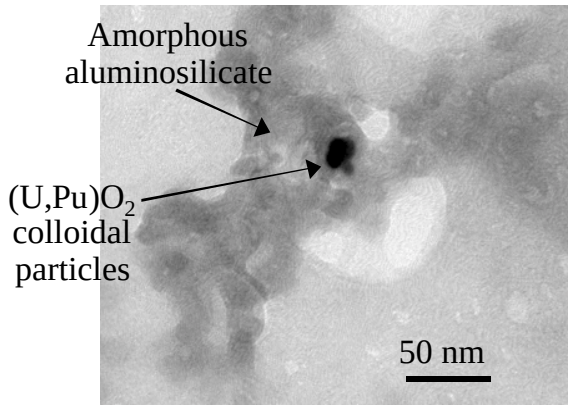
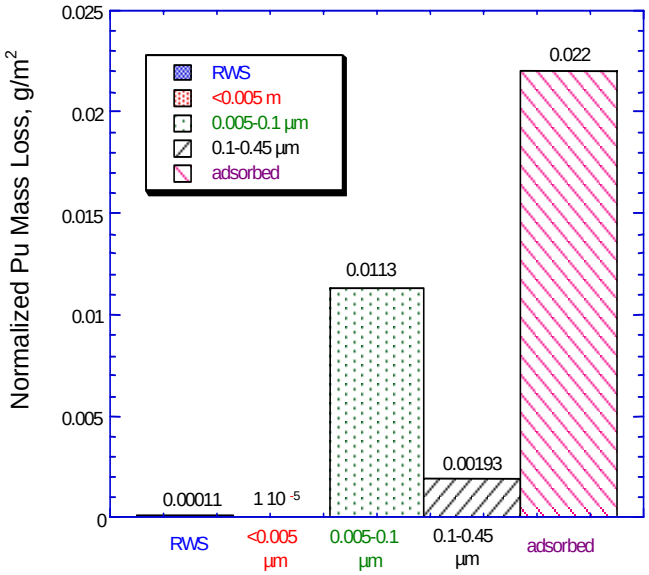


Transmission Electron Micrograph of $(U,Pu)O_2$ and Amorphous Aluminosilicate Colloidal Particles Released after 28 Days in 120˚C PCT of Ceramic Waste Form



Normalized Plutonium Mass Losses after 7 Days in 120˚C PCT with Ceramic Waste Form. Bars show rapid water soluble (RWS), sequential filtrate, and adsorbed fractions. Averaged from triplicate tests.